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**(54) PALELY COLORED GLASS HAVING HIGH TRANSMITTANCE AND METHOD FOR  
PRODUCING THE SAME**

(57) The present invention provides a light-colored high-transmittance glass sheet including, as coloring components, in weight percent, less than 0.06% total iron oxide in terms of  $Fe_2O_3$  (T- $Fe_2O_3$ ); 0.5 to 5ppm CoO; and 0 to 0.45% cerium oxide; wherein the ratio of FeO in terms of  $Fe_2O_3$  to T- $Fe_2O_3$  is less than 40%; and wherein the glass sheet has a dominant wavelength of

470 to 495nm when measured at a glass sheet thickness of 10mm. The present invention also provides a light-colored high-transmittance glass sheet of light neutral gray or bronze tint with a dominant wavelength of 560 to 585nm.

**EP 1 201 615 A1**

**Description****Technical Field**

5 [0001] The present invention relates to a light-colored high-transmittance glass having a light blue, neutral gray or bronze tint and high transmittance, that is suitable as a building glass or interior glass, and to a method for manufacturing such a glass at low cost.

**Background Art**

10 [0002] Recently, so-called crystal clear glass that is substantially colorless has been favored for exterior or interior use in buildings. But there are also cases in which light blue, gray or bronze glass is preferred in order to provide balance with the tints of the surrounding interior and exterior.

15 [0003] For this purpose, glass of light color and high transmittance is used, which is obtained by using raw materials of high purity, in which the iron content has been reduced considerably compared to that in regular soda-lime-based glass composition, or by adding small amounts of coloring agents to the glass.

20 [0004] For example, the edge colored (high transmittance) glass disclosed in JP H04-228450A is a soda-lime glass containing (in weight percent) less than 0.02% total iron oxide in terms of  $Fe_2O_3$  as a coloring agent, and the ratio of the ferrous iron ( $FeO$ ) to the total iron oxide is at least 0.4, whereby a luminous transmittance (when measured with the CIE Standard illuminant C) of at least 87% is attained at a thickness of 5.66mm, yielding a glass with slight color and high transmittance.

25 [0005] This glass composition is characterized in that, in order to attain the above properties, it has a small  $SO_3$  content, a manufacturing method is used in which the melting includes separate liquefying and refining steps, and a batch material is used that does not contain limestone or dolomite, so as to lower the iron content in the glass.

30 [0006] In the edge-colored high transmittance glass disclosed in JP H04-228451A, trace amounts of Se and  $CoO$  are added to a glass composition containing about the same amount of iron oxide, so as to obtain a glass sheet with a dominant wavelength in transmission of 570 to 590nm, in which the edge color (of the glass) harmonizes with wood colors.

35 [0007] On the other hand, methods have been proposed, in which the coloring of soda-lime glass containing a normal amount of iron oxide impurities is reduced by changing the basic composition of the glass.

40 [0008] For example, in accordance with the transparent glass composition for manufacturing window glass disclosed in JP H08-40742A, a soda-lime-silica glass in which the total amount of iron oxide in terms of ferric oxide accounts for 0.02 to 0.2wt% includes as a basic composition, in weight percent, 69 to 75%  $SiO_2$ , 0 to 3%  $Al_2O_3$ , 0 to 5%  $B_2O_3$ , 2 to 10%  $CaO$ , less than 2%  $MgO$ , 9 to 17%  $Na_2O$ , 0 to 8%  $K_2O$ , arbitrary amounts of fluorine, zinc oxide, zirconium oxide, less than 4wt% of barium oxide and not more than 10wt% of the alkaline earth metal oxides. According to this composition, the  $FeO$  absorption band can be shifted to longer wavelengths, or the gradient of the  $FeO$  absorption band at the edge of the visible spectrum near infrared can be made steeper. This makes it possible to manufacture a window glass with superior infrared absorption and with less coloring than soda-lime-silica glasses having a normal basic composition.

45 [0009] However, in the edge-colored high transmittance glasses disclosed in JP H04-228450A and JP H04-228451A, it is a precondition that limestone and dolomite, which contain relatively large amounts of iron oxide impurities, cannot be used, so as to control the total iron oxide in terms of  $Fe_2O_3$  included as the coloring agent to less than 0.02wt%. Therefore, it is necessary to use special raw materials such as calcium carbonate minerals or hydrated aluminum containing less iron oxide, which makes the resulting glass more expensive.

50 [0010] In the edge-colored high transmittance glass disclosed in JP H04-228450A, to obtain a desired pure bright azure edge color, it is necessary to make the ratio of ferrous iron ( $FeO$ ) to the total iron oxide at least 0.4.

55 [0011] Therefore, it is desirable to apply a special manufacturing method, in which the method includes separate melting and refining steps, and to suppress the  $SO_3$  content to a low level, which makes the resulting glass more expensive.

50 [0012] If, in the glasses disclosed in these publications, the raw materials for the glass contain  $Ni$  ions as impurities, then the  $Ni$  ions tend to bond with sulfide ions, forming  $NiS$ , which could cause spontaneous breakage. This is because the amount of  $Fe$  ions, which bond more easily with sulfide ions than  $Ni$  ions, is suppressed so as to attain a light tint.

55 [0013] In the transparent glass composition for manufacturing window glass disclosed in JP H08-40742A, the transmittance of soda-lime glass containing a normal amount of iron oxide is increased by changing the basic composition of the glass.

[0014] However, the effect of the method disclosed in this publication, that is, the degree that the  $FeO$  absorption is shifted to longer wavelengths, is insufficient for building or interior glass, for which a light tint is desired.

[0015] Moreover, in the composition disclosed in this publication, the amounts of  $MgO$  and  $MgO + CaO$  are less,

and to compensate the adverse effect this has on the melting, the amount of  $\text{Na}_2\text{O}$  is increased to more than the normal amount, so that this composition is not suitable for mass production due to the high liquidus temperature and the high costs.

5 [0016] The effect disclosed in this publication can be enhanced by adding such components as  $\text{F}$  or  $\text{BaO}$ , but adding these components is not desirable, as it increases the costs, and the volatility of the  $\text{F}$  shortens the furnace lifetime and leads to emission of hazardous substances into the atmosphere.

Disclosure of the Invention

10 [0017] In view of the problems of the related art, it is an object of the present invention to provide a light-colored high-transmittance glass, in particular a glass having high transmittance and a tint of light blue, neutral gray or bronze that is suitable as building glass or interior glass, as well as a method for manufacturing such a glass at low cost.

[0018] According to one aspect of the present invention, a light-colored high-transmittance glass sheet containing 15 silica as a main component is characterized in that

the glass sheet includes, as coloring components, in weight percent:

less than 0.06% total iron oxide (referred to as "T- $\text{Fe}_2\text{O}_3$ " in the following) in terms of  $\text{Fe}_2\text{O}_3$ ;

0.5 to 5ppm  $\text{CoO}$ ;

0 to 0.45% cerium oxide;

20 wherein the ratio of  $\text{FeO}$  in terms of  $\text{Fe}_2\text{O}_3$  to T- $\text{Fe}_2\text{O}_3$  (referred to as "FeO ratio" in the following) is less than 40%; and

wherein the glass has a light blue tint with a dominant wavelength of 470 to 495nm when measured with the CIE Standard illuminant C at a glass sheet thickness of 10mm.

25 [0019] It is preferable that the light-colored high-transmittance glass sheet with light blue tint in accordance with the present invention includes, in weight percent, less than 2ppm  $\text{CoO}$  and at least 0.02% T- $\text{Fe}_2\text{O}_3$ .

[0020] It is preferable that the dominant wavelength of a light-colored high-transmittance glass sheet with light blue tint in accordance with the present invention is 480 to 490nm.

30 [0021] According to another aspect of the present invention, a light-colored high-transmittance glass sheet containing silica as a main component is characterized in that the glass sheet includes, as coloring components, in weight percent:

at least 0.02% and less than 0.06% T- $\text{Fe}_2\text{O}_3$ ;

0.25 to 3ppm  $\text{Se}$ ;

0 to 3ppm  $\text{CoO}$ ;

35 0 to 0.45% cerium oxide;

wherein the FeO ratio is less than 40%; and

wherein the glass has a light neutral gray or bronze tint with a dominant wavelength of 560 to 585nm when measured with the CIE Standard illuminant C at a glass sheet thickness of 10mm.

40 [0022] It is preferable that the light-colored high-transmittance glass sheet with light neutral gray or bronze tint in accordance with the present invention includes, in weight percent, 0.5 to 2ppm  $\text{Se}$ , and 0.5 to 1ppm  $\text{CoO}$ .

[0023] It is preferable that the dominant wavelength of a light-colored high-transmittance glass sheet with light neutral gray and bronze tint in accordance with the present invention is 565 to 580nm.

45 [0024] It is preferable that in the light-colored high-transmittance glass sheet with a light neutral gray tint of the present invention, at a thickness of 10mm, the chromaticities  $a^*$  and  $b^*$  in the  $L^*a^*b^*$  color system measured with the CIE Standard illuminant C are  $-1 \leq a^* \leq 0.5$  and  $-0.5 \leq b^* \leq 1.5$ .

[0025] In the above aspects of the present invention, it is preferable that the content of cerium oxide, expressed in weight percent, is less than 0.1%.

50 [0026] In the light-colored high-transmittance glasses with the afore-mentioned preferable coloring agent compositions and tints, it is preferable that the basic glass comprises, in weight percent:

65 to 80%  $\text{SiO}_2$ ;

0 to 5%  $\text{Al}_2\text{O}_3$ ;

more than 2%  $\text{MgO}$ ;

55 5 to 15%  $\text{CaO}$ ;

10 to 18%  $\text{Na}_2\text{O}$ ;

0 to 5%  $\text{K}_2\text{O}$ ;

5 to 15%  $\text{MgO} + \text{CaO}$ ;

10 to 20%  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ; and  
0.05 to 0.25%  $\text{SO}_3$ .

It is more preferable that it comprises, in weight percent,  
 5 more than 10%  $\text{MgO} + \text{CaO}$ ; and  
 more than 0.1%  $\text{SO}_3$ .

[0027] It is preferable that the glass is substantially free of fluorine, barium oxide and strontium oxide.

[0028] In the present invention, if Ni ion impurities are contained in the raw material by reducing the Fe ions, then the Ni ions tend to bond with the sulfide ions, forming  $\text{NiS}$ , which could cause spontaneous breakage. This is because the Ni ions are reduced, which bond more easily with sulfide ions than Ni ions, so as to attain a light tint.

[0029] This tendency can be countered by adding in the composition an oxide of a heavy element, such as Y, La, Zr, Hf, Nb, Ta, W, Zn, Ga, Ge and Sn, alone or in combination. These heavy element oxides do not color the glass, and have no harmful effect on the glass, even when it is exposed to a reducing atmosphere in the float bath.

[0030] It is preferable that the amount of heavy element oxide included alone or in combination is, in weight %, 0.001 to 1%, more preferably 0.01 to 0.1%, and most preferably 0.01 to 0.05%. Preferable heavy element oxides include  $\text{ZnO}$ .

[0031] When manufacturing the light-colored high-transmittance glass of the present invention, it is preferable to use dolomite and limestone as raw materials, as for normal soda-lime glass, because this minimizes cost increases for the glass sheet. This becomes possible by setting the iron oxide content within the above-noted preferable ranges.

[0032] In order to minimize cost increases for the glass in this melting method, as above, it is preferable that the batch material is melted in a top-heating tank-type furnace, in which the melting step and the refining step can be performed in one tank, which is routinely used for soda-lime glass melting furnaces.

[0033] The following is an explanation of the reasons for the composition limitations of the light-colored high-transmittance glass of the present invention. The following compositions are given in weight percent.

[0034] In a glass composition, iron oxide is present in form of  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$ . The  $\text{Fe}_2\text{O}_3$  component adds a very light yellow tint to the glass, while the  $\text{FeO}$  component adds a blue tint to the glass.

[0035] In order to obtain the desired light tint and high transmittance, the  $\text{T-Fe}_2\text{O}_3$  has to be less than 0.06% and the  $\text{FeO}$  ratio has to be in a range less than 40%. If the  $\text{T-Fe}_2\text{O}_3$  is not less than 0.06%, then the green coloring caused by the included iron oxide becomes too dark, and it becomes difficult to attain the desired tint. A preferable upper limit for the  $\text{T-Fe}_2\text{O}_3$  is 0.04%, at which the green color is not very perceptible and a high transmittance is obtained. If the  $\text{FeO}$  ratio is not less than 40%, then the melting in a regular melting furnace for soda-lime glass becomes difficult.

[0036] If the  $\text{T-Fe}_2\text{O}_3$  is less than 0.02%, then it is necessary to use high-purity raw materials with little iron content, which increases the costs considerably, so that it is preferable that the amount of  $\text{T-Fe}_2\text{O}_3$  is at least 0.02%.

[0037] In order to attain a blue tint,  $\text{CoO}$  is an essential component. If less than 0.5ppm are included, then the green tint of the iron oxide is conspicuous, and if more than 5ppm are included, then the blue is too strong. A more preferable range is not more than 2ppm.

[0038] In order to attain a neutral gray or bronze tint,  $\text{Se}$  is an essential component while  $\text{CoO}$  is an arbitrary component. To attain a neutral gray or bronze tint, it is very important to balance the green color of the iron oxide, the reddish brown color of the  $\text{Se}$ , and the blue color of the  $\text{CoO}$ . If the  $\text{Se}$  is less than 0.25ppm, then the tint takes on a somewhat greenish color, and if the  $\text{Se}$  is more than 3ppm, then the reddish brown color becomes too strong and conspicuous. If the  $\text{CoO}$  is more than 3ppm, then the blue color becomes too strong and conspicuous, and it becomes difficult to attain a neutral gray or bronze tint. In order to attain a neutral gray or bronze tint while keeping the transmittance high, it is preferable that the  $\text{Se}$  is in the range of 0.5 to 2ppm and  $\text{CoO}$  is in the range of 0.5 to 1ppm.

[0039] The cerium oxide is not essential but advantageous for reducing the green color by oxidizing  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ , and also has the additional advantageous effect of decreasing the UV ray transmittance of the glass sheet. These effects increase as more cerium oxide is included, but when the upper limit of 0.45% is exceeded, its yellow color becomes conspicuous, and it becomes difficult to attain the desired tint. Furthermore, since it is an expensive material increasing the costs of the glass, it is preferable to add less than 0.1%.

[0040]  $\text{SiO}_2$  is the main component to form the glass network. If the  $\text{SiO}_2$  is less than 65%, then the durability of the glass decreases, and if it exceeds 80%, it becomes difficult to melt the glass.

[0041]  $\text{Al}_2\text{O}_3$  is a component that improves the durability of the glass. However, when more than 5%  $\text{Al}_2\text{O}_3$  is included, it becomes difficult to melt the glass. Preferably,  $\text{Al}_2\text{O}_3$  is included in the range of 0.1 to 2.5%.

[0042]  $\text{MgO}$  and  $\text{CaO}$  improve the durability of the glass, and also are used to adjust the liquidus temperature and viscosity during the forming. If not more than 2%  $\text{MgO}$  is included, the liquidus temperature increases. If less than 5% or more than 15%  $\text{CaO}$  is included, the liquidus temperature increases. If the total amount of  $\text{MgO}$  and  $\text{CaO}$  is less than 5%, the durability of the glass decreases, and if the total amount exceeds 15%, the liquidus temperature increases. If the total amount of  $\text{MgO}$  and  $\text{CaO}$  is small, for example not more than 10%, then it is necessary to increase the amount of  $\text{Na}_2\text{O}$  to compensate for the deterioration of the melting properties and the increase of the viscosity of the glass melt, which leads to cost increases and to a decrease in the chemical durability of the glass. Thus, it is preferable

that the total amount of MgO and CaO is more than 10%.

[0043] The components Na<sub>2</sub>O and K<sub>2</sub>O work as melting accelerators. If less than 10% Na<sub>2</sub>O is included or if the total amount of Na<sub>2</sub>O and K<sub>2</sub>O is less than 10%, then the effect of melt acceleration is poor. If Na<sub>2</sub>O exceeds 18% or the total amount of Na<sub>2</sub>O and K<sub>2</sub>O exceeds 20%, then the durability of the glass decreases. Since K<sub>2</sub>O is more expensive than Na<sub>2</sub>O, it is preferable that the included amount of K<sub>2</sub>O does not exceed 5%.

[0044] SO<sub>3</sub> is a component that enhances the refining of the glass. If less than 0.05% SO<sub>3</sub> is included, a sufficient refining effect cannot be attained with the usual melting methods. A preferable range for SO<sub>3</sub> is at least 0.1%. On the other hand, if more than 0.25% is included, the SO<sub>2</sub> generated from decomposition of SO<sub>3</sub> may remain in the glass as bubbles and bubbles tend to be generated by reboiling.

[0045] TiO<sub>2</sub> is not an essential component, but it can be added to improve the UV ray absorption, in a suitable amount within a range that does not damage the optical properties of the object of the present invention. If too much TiO<sub>2</sub> is added, the glass takes on a yellowish color, so that it is preferable to set the included TiO<sub>2</sub> in a range of not more than 0.2%.

[0046] Furthermore, the effect of the present invention is not harmed by including fluorine, barium oxide or strontium oxide. However, these components have undesirable influences with regard to cost increases, furnace lifetime, and emission of hazardous substances into the atmosphere, so that it is preferable that the glass is substantially free of these components.

[0047] For the component to be added as an oxidizing agent to the glass with a composition in the above-described ranges, cerium oxide in the above-defined range is preferable in view of its additional preferable effect of UV ray absorption. However, it is also possible to add other oxidizing agents, such as manganese oxide, in a range of not more than 1%, alone or in combination with the cerium oxide.

[0048] The oxide of a heavy element, such as Y, La, Zr, Hf, Nb, Ta, W, Zn, Ga, Ge and Sn, is a component that does not have to be added in particular if the glass is used without tempering, but if the glass is used as a tempered glass that is reinforced by rapidly air-cooling, then it is preferable to add 0.001 to 1% of this component, alone or in combination of a plurality of these heavy element oxides, so as to prevent spontaneous breakage due to the NiS. At less than 0.001%, the effect of preventing the generation of NiS is weak, and at not less than 1%, the costs for the raw materials become high and the glass tends to be devitrified. A more preferable addition range is 0.01 to 0.1%, and a most preferable addition range is 0.01 to 0.05%. Furthermore, all of the above-mentioned heavy element oxides have more or less the same effect of preventing the generation of NiS, but ZnO is most preferable in view of its effect and costs.

[0049] Moreover, as the raw material for these heavy element oxides, it is also possible to use non-oxide materials such as sulfates or nitrates if the materials turn into an oxide during the melting of the glass.

[0050] Moreover, it is also possible to add for example at least one of Cr<sub>2</sub>O<sub>3</sub>, NiO, V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub> as a regular coloring agent within a range that does not harm the light tint that is an object of the present invention. However, since the addition of such coloring agents strengthens the color tone and darkens the glass, it is preferable that the glass is substantially free from such coloring agents.

#### Embodiments of the Invention

[0050] The following is an explanation of the preferred embodiments of the present invention, with reference to specific examples.

#### Examples 1 to 5

[0051] The raw materials for the composition shown in Table 1 (in weight percent in terms of the oxides) were mixed using low-iron silica, limestone, dolomite, soda ash, saltcake, cerium oxide, CoO, metallic selenium and a carbonaceous reducing agent, and the batch material was heated to 1450°C in an electric furnace and melted. After four hours of melting, the glass material was poured onto a stainless steel plate, annealed to room temperature, and a glass sheet of about 15mm thickness was obtained. The concentrations in the table are given in weight percent, whereas only CoO and Se are given in ppm.

[0052] Then, the glass sheet was ground and polished to a thickness of 10mm, and for the optical properties, visible light transmittance, dominant wavelength, excitation purity, chromaticities a\* and b\* under the L\*a\*b\* color system were measured with the CIE Standard illuminant C, and solar radiation transmittance, and UV ray transmittance according to ISO 9050 were measured. Table 1 shows the optical properties of the resulting samples.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
SiO <sub>2</sub>	72.1	71.2	71.7	71.2	7.12
Al <sub>2</sub> O <sub>3</sub>	1.74	1.66	1.68	1.75	1.66
MgO	4.2	4.2	4.4	4.2	4.2
CaO	8.5	8.5	8.8	8.5	8.5
Na <sub>2</sub> O	13.0	13.5	12.5	13.1	13.5
K <sub>2</sub> O	0.7	0.7	0.7	1.0	0.7
SO <sub>3</sub>	0.12	0.20	0.15	0.18	0.20
T-Fe <sub>2</sub> O <sub>3</sub>	0.018	0.025	0.025	0.030	0.036
TiO <sub>2</sub>	0.02	0.02	0.04	0.04	0.02
cerium oxide	0	0	0.08	0	0
CoO	0.5	1	1.75	1	1
Se	0	0	0	0.75	2
FeO	0.006	0.007	0.003	0.008	0.009
FeO ratio	37	31	13	30	28
visible light transmittance (%)	90.4	88.9	91.0	87.8	85.9
solar radiation transm. (%)	88.4	84.8	90.5	84.0	83.8
UV ray transmittance (%)	67.6	63.8	36.7	55.2	53.8
dominant wavelength (nm)	488	485	480	570	577
excitation purity (%)	0.39	1.03	1.85	1.40	2.06
a*	-	-	-	-0.60	-0.10
b*	-	-	-	1.05	2.12

[0053] As becomes clear from Table 1, in the samples of the Examples 1 to 3, the glass has a clear light blue tint, as can be seen from the dominant wavelength, which is in the range of 480 to 490nm. In Example 4, the glass has an approximately neutral gray color, as can be seen from the chromaticities a\* and b\*. In Example 5, the glass has a light bronze tint, as can be seen from the dominant wavelength and the chromaticities a\* and b\*.

#### Comparative Examples 1 to 3

[0054] Table 2 lists the composition and optical properties of the comparative examples contrasted with the present invention. The compositions are given in weight percent.

Table 2

	Comp. Ex. 1	Comp Ex. 2	Comp. Ex. 3
SiO <sub>2</sub>	71.7	71.2	71.7
Al <sub>2</sub> O <sub>3</sub>	1.70	1.66	1.68
MgO	4.2	4.2	4.3
CaO	8.5	8.5	8.8
Na <sub>2</sub> O	13.0	13.5	12.5
K <sub>2</sub> O	0.7	0.7	0.7
SO <sub>3</sub>	0.16	0.20	0.20

Table 2 (continued)

	Comp. Ex. 1	Comp Ex. 2	Comp. Ex. 3
T- $\text{Fe}_2\text{O}_3$	0.018	0.025	0.080
$\text{TiO}_2$	0.02	0.02	0.04
FeO	0.006	0.008	0.020
FeO ratio	37	36	28
visible light transmittance (%)	90.6	90.3	86.0
solar radiation transm. (%)	88.6	86.8	75.4
UV ray transmittance (%)	67.2	65.1	48.3
dominant wavelength (nm)	538	498	503
excitation purity (%)	0.36	0.53	1.01
a*	-	-	-2.31
b*	-	-	0.23

20 [0055] Comparative Examples 1 and 2 have the same basic composition of the present invention and include total iron oxide and a FeO ratio within the prescribed limit, but do not include Se or CoO. Comparative Example 3 is a typical 5 soda-lime glass composition.

[0056] As can be seen from the fact that in all of these compositions the dominant wavelength is in the range of 498 to 538nm, these compositions yield colors ranging from bluish green to yellowish green, which is different from the 10 blue, neutral gray or bronze that is the intended object of the present invention. Comparative Examples 1 and 2 have a light tint, and their transmittance is relatively high, but in some cases, they take on an undesirable greenish yellow tint. Moreover, the typical soda-lime glass of the Comparative Example 3 has a dark green color, as can be seen from 15 the fact that the value a\* in the L\*a\*b\* color system is -2.31, so that it is not suitable for applications necessitating a light tint.

20 [0057] Then, regarding the creation of NiS in a float furnace, the following experiment was performed.

#### Examples 6 to 10

25 [0058] The same basic compositions as in the Examples 1 to 5 were prepared, leading to the compositions listed in Table 3 (expressed in weight percent in terms of the oxides), and the oxide of a heavy element was added and mixed. Zinc nitrate hexahydrate was added only for Zn. Then, 0.028g Ni powder with an average particle diameter of 149 $\mu\text{m}$  was added per 200g of this mixture in the molten glass, provided in an alumina crucible with 250cm<sup>3</sup> capacity, which 30 was pre-heated for 30min at 600°C, and then put into an electric furnace at 1370°C and heated in 10min to 1400°C. Then, after keeping it at this temperature for 2.2 hours, the crucible was retrieved from the furnace, its content was 35 cast out, and annealed from 650°C to room temperature, thus producing the Examples 6 to 10.

[0059] In the resulting glass samples, the number of NiS particles in the glass was counted with a stereoscopic 40 microscope, and the number of NiS particles per 100g of glass was calculated. The result is shown in Table 4.

#### Reference Examples 1 to 5

45 [0060] Samples of the same composition as in the Examples 6 to 10 was prepared, except that no heavy element oxide was added, and as in the Examples 6 to 10, the mixtures were melted, cast out, and annealed, thus producing the Reference Examples 1 to 5. Again, the number of NiS particles per 100g of glass was calculated; the results are 50 shown in Table 5.

Table 3

	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
base composition	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
heavy element oxide	ZnO	ZnO	La <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	WO <sub>3</sub>
addition amount (ppm)	200	400	1000	500	100

Table 4

	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10
number of NiS particles	9	4	9	11	13

5

Table 5

	Ref. Ex. 1	Ref. Ex. 2	Ref. Ex. 3	Ref. Ex. 4	Ref. Ex. 5
number of NiS particles	43	32	23	30	28

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[0061] From the results in Tables 4 and 5, it can be seen that the generation of NiS particles can be suppressed by addition of the oxides listed in Table 3.

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[0062] As detailed above, in accordance with the light-colored high-transmittance soda-lime glass of the present invention, it is possible to provide an inexpensive glass having high transmittance and a tint of light blue, neutral gray or bronze.

[0063] The light-colored high-transmittance glass of the present invention is particularly suitable as building glass.

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[0064] The invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not limiting. The scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

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### Claims

1. A light-colored high-transmittance glass sheet containing silica as a main component, characterized in that the glass sheet comprises the following coloring components, in weight percent:

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less than 0.06% T- $\text{Fe}_2\text{O}_3$ , wherein T- $\text{Fe}_2\text{O}_3$  is total iron oxide in terms of  $\text{Fe}_2\text{O}_3$ ;  
0.5 to 5ppm CoO; and  
0 to 0.45% cerium oxide;

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wherein the ratio of FeO in terms of  $\text{Fe}_2\text{O}_3$  to T- $\text{Fe}_2\text{O}_3$  is less than 40%; and  
wherein the glass sheet has a dominant wavelength of 470 to 495nm when measured with the CIE Standard Illuminant C at a glass sheet thickness of 10mm.

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2. The light-colored high-transmittance glass sheet according to Claim 1, characterized in that the glass sheet comprises, in weight percent, at least 0.5ppm and less than 2ppm CoO.

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3. The light-colored high-transmittance glass sheet according to Claim 1, characterized in that the glass sheet comprises, in weight percent, at least 0.02% T- $\text{Fe}_2\text{O}_3$ .

4. A light-colored high-transmittance glass sheet containing silica as a main component, characterized in that the glass sheet comprises the following coloring components, in weight percent:

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at least 0.02% and less than 0.06% T- $\text{Fe}_2\text{O}_3$ , wherein T- $\text{Fe}_2\text{O}_3$  is total iron oxide in terms of  $\text{Fe}_2\text{O}_3$ ;  
0.25 to 3ppm Se;  
0 to 3ppm CoO; and  
0 to 0.45% cerium oxide;

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wherein the ratio of FeO in terms of  $\text{Fe}_2\text{O}_3$  to T- $\text{Fe}_2\text{O}_3$  is less than 40%; and  
wherein the glass sheet has a dominant wavelength of 560 to 585nm when measured with the CIE Standard Illuminant C at a glass sheet thickness of 10mm.

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5. The light-colored high-transmittance glass sheet according to Claim 4, characterized in that the glass sheet comprises, in weight percent, 0.5 to 2ppm Se, and 0.5 to 1ppm CoO.

6. The light-colored high-transmittance glass sheet according to Claim 4, characterized in that, at a glass sheet thickness of 10mm, the chromaticities  $a^*$  and  $b^*$  in L\* $a^*$  $b^*$  color system measured with the CIE Standard illuminant C are  $-1 \leq a^* \leq 0.5$  and  $-0.5 \leq b^* \leq 1.5$ .
- 5 7. The light-colored high-transmittance glass sheet according to Claim 1 or 4, characterized in that the glass sheet comprises, in weight percent, less than 0.1% cerium oxide.
8. The light-colored high-transmittance glass sheet according to Claim 1 or 4, characterized in that the glass sheet comprises the following basic glass composition, in weight percent:
  - 10 65 to 80%  $\text{SiO}_2$ ;
  - 0 to 5%  $\text{Al}_2\text{O}_3$ ;
  - more than 2%  $\text{MgO}$ ;
  - 5 to 15%  $\text{CaO}$ ;
  - 15 10 to 18%  $\text{Na}_2\text{O}$ ;
  - 0 to 5%  $\text{K}_2\text{O}$ ;
  - 5 to 15%  $\text{MgO} + \text{CaO}$ ;
  - 10 to 20%  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ; and
  - 0.05 to 0.25%  $\text{SO}_3$ .
- 20 9. The light-colored high-transmittance glass sheet according to Claim 8, characterized in that the glass sheet comprises, in weight percent:
  - the glass sheet comprises, in weight percent:
  - more than 10%  $\text{MgO} + \text{CaO}$ ; and
  - more than 0.1%  $\text{SO}_3$ .
- 25 10. The light-colored high-transmittance glass sheet according to Claim 1 or 4, characterized in that the glass is substantially free of fluorine, barium oxide and strontium oxide.
11. The light-colored high-transmittance glass sheet according to Claim 1 or 4, characterized in that the glass comprises, in weight percent, 0.001 to 1% heavy element oxide;
  - 30 wherein the heavy element is at least one element selected from the group consisting of Y, La, Zr, Hf, Nb, Ta, W, Zn, Ga, Ge and Sn.
12. The light-colored high-transmittance glass sheet according to Claim 11, characterized in that the glass comprises, in weight percent, 0.01 to 0.1% heavy element oxide.
- 35 13. The light-colored high-transmittance glass sheet according to Claim 12, characterized in that the glass comprises, in weight percent, 0.01 to 0.05% heavy element oxide.
14. The light-colored high-transmittance glass sheet according to Claim 11, characterized in that the heavy element oxide is  $\text{ZnO}$ .
- 40 15. A method for manufacturing the light-colored high-transmittance glass in accordance with Claim 1 or 4, characterized in that dolomite and limestone are included in the raw materials for the light-colored high-transmittance glass.
- 45 16. The method according to Claim 15, comprising melting batch material of the raw material in a top-heating tank-type melting furnace.

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INTERNATIONAL SEARCH REPORT		International application No. PCT/JP01/01609
<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl' C03C4/02, C03C9/095		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl' C03C1/00-14/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX PA	JP, 2000-143283, A (Flachglas AG), 23 May, 2000 (23.05.00), Full text & DE, 29819347, U1	1-3, 7, 10, 15, 16 4-6, 8, 9, 11-14
A	JP, 10-045424, A (Central Glass Co., Ltd.), 17 February, 1998 (17.02.98), Full text (Family: none)	1-3, 7-16
A	US, 5030593, A (PPG Industries, Inc.), 09 July, 1991 (09.07.91), Full text & JP, 04-228451, A Full text & EP, 463606, A1	1-16
A	US, 5656559, A (Saint-Gobain Vitrage), 12 August, 1997 (12.08.97), Full text & JP, 08-040742, A, Full text & EP, 688741, A1 & FR, 2721600, A1	4-16
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 28 May, 2001 (28.05.01)	Date of mailing of the international search report 05 June, 2001 (05.06.01)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

International application No.

PCT/JP01/01609

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
  
  
  
  
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
  
  
  
  
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Of the inventions according to claims 1 to 16, inventions according to claims 1 to 3 and 7 to 16 (or inventions according to claims 1 to 3) relate to a palely colored glass having a high transmittance which has a dominant wave length of 470 to 495 nm and comprises CoO as an essential component. Whereas, the inventions according to claims 4 to 6 (or the inventions according to claims 4 to 16) relate to a palely colored glass having a high transmittance which has a dominant wave length of 560 to 585 nm, and does not comprise CoO as an essential component and comprises Se as an essential component. There is no technical relationship among those inventions involving one or more of the same or corresponding special technical features, and accordingly those inventions are not so linked as to form a single general inventive concept.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
  
  
  
  
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest  The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.